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CROSSLINKED RESIN AND PROCESS FOR THE MANUFACTURE OF  
OXIDES USING THIS CROSSLINKED RESIN

The field of the invention is that of thin layer oxides  
5 and more specifically of oxides in the glass or ceramic  
form obtained by sol-gel processes.

Conventionally, the sol-gel process makes it possible,  
starting from a colloidal solution based on metal  
10 alkoxides or on silicon alkoxide, to manufacture  
powders or thin layers of oxides in the glass or  
ceramic form.

More specifically, the alkoxides are dissolved in a  
15 solvent and their hydrolysis leads to the condensation  
of polymeric networks of oxides and hydroxides.  
Nevertheless, it is not easy to control the degree and  
the kinetics of hydrolysis when synthesizing complex  
phases comprising a large number of components with  
20 different properties.

It is possible with difficulty to control  
simultaneously the chemical homogeneity which makes it  
possible to lower the synthesis temperature and the  
25 rheology, desirable for producing thin layer  
deposition.

It is possible to modify the viscosity and the  
elasticity of the solutions prepared by addition of  
30 agents, such as polyalcohols or polyacids, resulting in  
polymer resins. However, these additives are not  
necessarily compatible with cations and result in  
solutions with an adhesion to substrates which is not  
well suited to depositions, by centrifuging or by  
35 dipping, on substrates.

In this context, the Applicant Company has filed a  
patent application, published under the number 431 999,  
providing a process for the deposition of a ceramic

composition as a thin layer starting from a homogeneous solution, the rheology of which can be adjusted to deposition by centrifuging or dipping. The cations are dissolved in a solution where polymerization (or maturation) is brought about by the reaction of two organic compounds: acetylacetone (ACAC) and hexamethylenetetramine (HMTA).

More specifically, these two compounds, brought into contact under hot conditions with an acid, result in a polymeric species. The combination thus formed is thus a binder comprising metal oxide grains.

This resin can subsequently be deposited on a substrate, to be brought to high temperature and to result in the production of a thin layer ceramic.

More specifically, the resin deposited on the substrate is first of all brought to a calcination temperature of the order of 500°C. During this operation, the solvent is evaporated and certain chemical entities are calcined to produce amorphous oxides.

25 A rapid annealing operation at approximately 700°C is  
then carried out to produce the desired crystalline  
phase of the corresponding ceramic.

During the calcination operation, numerous stresses are generated due to the evaporation of the solvent and to the calcination of certain chemical compounds.

The invention provides for the use of a crosslinked resin which can be subsequently calcined, so as to reduce the stresses occasioned during this heating, for the manufacture of ceramic or of glass.

Furthermore, this crosslinked resin makes it possible to obtain in a very direct manner ceramic patterns with

very small dimensions in comparison with the solutions of the prior art.

This is because the resin disclosed in Patent  
5 Application No. 431 999 can advantageously be exposed to ultraviolet radiation to result in a crosslinked resin with an improved performance.

This is why a subject matter of the invention is more  
10 specifically a crosslinked resin, characterized in that it comprises a material obtained from the mixing of one or more simple metal alkoxides, complex metal alkoxides or silicon alkoxides, of acetylacetone and of hexamethylenetetramine, and then heating said mixture and  
15 exposing it to radiation.

According to an alternative form of the invention, the simple metal alkoxides are of titanium alkoxide or zirconium alkoxide type.

20 According to another alternative form of the invention, the complex metal alkoxide is prepared from lead carboxylate, from titanium alkoxide and from zirconium alkoxide.

25 According to an alternative form of the invention, the mixture additionally comprises photoinitiating agents for enhancing the performance of the crosslinked resin obtained.

30 These agents can in particular be radical photoinitiators of Irgacure 184 or 1800 type from Ciba or alternatively benzophenone or diphenyl ketone.

35 According to an alternative form of the invention, the solvent is of 2-ethylhexanol and/or acetic acid type.

Another subject matter of the invention is a process for the manufacture of a ceramic or of a glass comprising:

- the preparation of a solution of metal alkoxides in acetylacetone;
- the production of a photosensitive resin by reaction under hot conditions of an acid and of hexamethylenetetramine with said solution;
- the deposition of the photosensitive resin on a substrate;
- the exposure of the photosensitive resin to ultraviolet radiation;
- the calcination of the crosslinked resin.

15      The exposure of the photosensitive resin to ultraviolet radiation results in a denser gel and thus in thicker glass or ceramic oxide layers than according to the prior art.

20      According to an alternative form of the invention, the substrate is glass.

A further subject matter of the invention is a process for the manufacture of ceramic or glass patterns at the surface of a substrate, characterized in that:

- exposure to radiation is carried out through a mask, so as to define radiation-exposed patterns and non-radiation-exposed patterns;
- it comprises the dissolution of the non-radiation-exposed patterns in a solvent.

Such ceramic patterns are used in particular in such applications as ferroelectric memories, integrated capacitors, pyroelectric detectors for imaging or 35 infrared detection, or piezoelectric sensors and microsystems.

This is why a final subject matter of the invention is components of capacitor, piezoelectric transducer or

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piezoelectric memory type obtained from the process for the manufacture of a ceramic or of a glass according to the invention.

5 According to the prior art, it is possible to deposit a layer of oxide at the surface of a substrate by means of processes of cathodic sputtering type or a metalorganic chemical vapor deposition (MOCVD) process and then to define patterns on said layer of oxide by  
10 means of conventional photolithographic processes.

Thus, a photosensitive resin can be deposited at the surface of a ceramic layer prepared beforehand at the surface of a substrate. Said photosensitive resin is  
15 exposed to radiation through a mask and then the radiation-exposed or non-radiation-exposed resin (according to whether a negative or positive resin is involved) is dissolved using a solvent. The various stages of a photolithographic process which makes it  
20 possible to define ceramic patterns are illustrated in figure 1.

More specifically, figure 1a represents a ceramic layer 1 on a substrate 0, which substrate is covered  
25 with a layer of photosensitive resin 2. Figure 1b diagrammatically represents the photosensitive resin 2 exposed to radiation through a mask 3. The radiation-exposed parts of the resin may become insoluble in some solvents, whereas the non-radiation-exposed parts  
30 remain soluble in said solvents. A mask is thus defined which makes it possible, for example, to etch the unmasked parts of figure 1c, with an acid of HCl/HF type in the case of a fine PZT layer, to produce the patterns illustrated in figure 1d. This chemical attack  
35 is isotropic and does not allow very fine resolution. Typically, it is difficult to produce patterns with a width of less than 10 µm.

The crosslinked resin according to the invention makes it possible to directly produce ceramic or glass patterns, dispensing with the need to use a masking resin and an isotropic etching process.

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A better understanding of the invention will be achieved and other advantages will become apparent on reading the description which will follow, given without implied limitation, and by virtue of the 10 appended figures, among which:

- figures 1a-1d illustrate the stages of a masking process according to the known art for defining ceramic patterns;
- figures 2a-2c illustrate the stages of a process 15 according to the invention for defining ceramic patterns;
- figures 3a and 3b illustrate a layer of metal oxides with a thickness of a few microns on a silicon substrate, before and after sintering;
- 20 - figures 4a and 4b illustrate patterns formed from metal oxides with a thickness of a few microns on a silicon substrate, before and after sintering, obtained according to the invention.

25 A description will now be given of the invention in the context of an example of lead, zirconium and titanium (PZT) oxide but the invention applies just as well to the manufacture of silica or of refractory oxides, such as  $TiO_2$  or  $ZrO_2$ . ✓

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First stage:

**Preparation of a solution A based on metal alkoxides**

35 1 mol of lead 2-ethylhexanoate, 0.5 mol of zirconium n-butoxide and 0.5 mol of titanium n-butoxide are mixed at 60°C. A heavy carboxylate, 2-ethylhexanoate, is chosen in order to obtain a resin sufficiently viscous for a deposition on the substrate leading to a sufficient thickness.

The preceding mixture is brought together with acetyl-acetone in a proportion of 1 mol of ACAC per mole of Pb.

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A solvent of heavy alcohol type, for example 2-ethyl-hexanol, can advantageously be added thereto to adjust the viscosity of said solution.

10 A solution A based on lead, zirconium and titanium oxides and on ACAC is thus obtained.

Second stage:

**Preparation of a solution B based on HMTA**

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At the same time, the mixture of 0.5 mol of hexamethylenetetramine (HMTA) in the presence of 100 cm<sup>3</sup> of acetic acid is prepared at 60°C. It is just as possible to replace acetic acid with propanoic acid or trifluoroacetic acid.

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Third stage:

**Preparation of a photosensitive resin based on metal alkoxides**

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The solutions A and B are brought together and are heated to form the resin.

30

Typically, heating can be carried out at 118°C for approximately 15 minutes. The higher the temperature, the more viscous the resin.

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A PZT resin is thus obtained in which the grains of PZT oxides are taken up in a polymer matrix formed from HMTA and ACAC.

Fourth stage:

**Exposure to radiation of the photosensitive resin to form the crosslinked resin**

The resin 11 formed in stage 3 can typically have a kinematic viscosity of the order of 25 centistokes and be deposited by conventional centrifuging or dipping  
5 means at the surface of a substrate 01 (figure 2a).

The resin is then exposed to ultraviolet radiation, typically at 335 nm, making it possible to densify the resin and to render it insoluble to certain solvents,  
10 including dilute acetic acid and/or 2-ethylhexanol.

Exposure to radiation can advantageously be carried out through a mechanical mask 31, so as to define soluble patterns 11 and insoluble patterns 12 in the resin  
15 layer (figure 2b).

It is particularly advantageous to define patterns formed from oxides prior to the firing or sintering stage corresponding to densification. The patterns  
20 soluble in 2-ethylhexanol and/or acetic acid are subsequently removed to leave in place only the insoluble patterns 12 (figure 2c).

This is because, according to the processes of the prior art, resin layers above a thickness of the order  
25 of 2 microns, deposited on plaques with a diameter of approximately 10 cm, for example, have a tendency to fail during the sintering stage because of the stresses generated between the layer and the substrate during  
30 the decrease in volume related to the change from a porous gel to a dense oxide. For the same reasons, the substrate can have a tendency to bend.

When the patterns are defined photochemically in the resin layer before sintering, the stresses are decreased for two reasons:

- the starting gel is denser because of the ultraviolet radiation;

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the area under which these stresses are exerted is smaller and the stresses can release over the edges of the pattern, as illustrated in figures 3 and 4, which respectively represent, figures 3a and 3b, an oxide layer 13 with a thickness of a few microns on a silicon substrate 03, before sintering and after sintering, and, figures 4a and 4b, patterns formed from oxides 14 prepared beforehand, with a thickness of a few microns, on a silicon substrate 04, before sintering and after sintering.

Typically, the ceramic patterns thus defined without deformation can just as easily have dimensions of less than a few microns as dimensions of a few tens, indeed even a few hundreds, of microns.

This is because, according to the invention, the stages of photolithography, exposure to radiation and then dissolution make it possible in particular to obtain very fine patterns, in contrast to the ceramic isotropic chemical etching operations of the prior art.